Feature Article

50th Anniversary Product

The 50 Series pH Meter

Takeshi Kobayashi

[The Development Team (Main body)]

Upper left:
Yuichi Ito

Back row from the left:
Seiichiro Yoshioka, Takeshi Shimizu, Hiroyuki Kitamura, Takeshi Mori, Yosuke Hisamori

Front row from the left:
Yoshiyuki Okada, Mitsuru Honjo, Yoshihiro Tarui, Katsuaki Ogura, Yoshihiko Ida

[The Development Team (Electrode)]

Back row from the left:
Yuji Nishio, Yasukazu Iwamoto, Nobuki Yoshioka, Shinji Takeichi, Takeshi Kobayashi, Kenichi Tanaka

Front row from the left:
Hiromi Ohkawa, Tsuyoshi Nakanishi, Satoshi Nomura, Hiroki Tanabe, Koji Ueda

In developing the 50 Series, we focused on the following two points: ease of use of the basic pH meter main unit and enhancement of the electrode performance as the most vital features for pH measurement. By adding a navigation function with character display, which is not used by conventional analyzers, as well as adopting the world's first color display, our new bench top pH meter has proved user friendly even for customers with no pH measurement knowledge. We took the World's top performing ToupH glass electrode series and succeeded in increasing the electrode life by improving the performance of the reference electrode and strengthening the durability of glass material. Also, the pH measurement field has been extended to new and unconventional measurement areas by commercialization of the glass-free ISFET electrode. This article describes features of this product in detail.

Introduction

This product is commercially manufactured as the 50 series and is a model change from the conventional D-20 series and F-20 series and commemorates HORIBA's 50th anniversary. In this development, a number of product lineups such as the pH meter main body, electrodes, and cleaning solution have been produced simultaneously. We have focused on developing user-friendly products common to all. We first decided the product concept by visiting a large number of customers before commencing development. Approximately a year and a half has now passed since the products were released, and we have received many favorable comments from our customers. The following are feature descriptions of each new product.

pH Meter Main Unit

This development has seen a total of 14 models of the D-50 series for on-site measurement and also the F-50 series for laboratory use, simultaneously produced in approximately one year, an unusually short period.

Portable pH Meter

The portable D-50 series pH meter has been produced for easier on-site use and is based on the conventional D-20 series. Figure 1 is a photo of the D-50 series, and Table 1 shows the main specifications.

Figure 1 The D-50 Series

Table 1 Main Specifications of the D-50 Series

		D-51	D-52	D-53	D-54	D-55
pH	Measurement method	Glass electrode method				
	Measurement range	pH 0.00 to 14.00				
	Repeatability	±0.01 pH ±1 digit				
mV (ORP)	Measurement range	-	-1999 to1999 mV			
	Repeatability	-	±1 mV ±1 digit			
Temperature	Measurement range	0.0 to 100.0 °C				
	Repeatability	±0.1 °C ±1 digit				
Ion	Measurement method	-	-	Ion selective electrode method	-	-
	Measurement range	-	-	0.00 µg/L to 999 g/L (mol/L)	-	-
	Repeatability	-	-	±0.5%F.S.±1 digit	-	-
Conductivity	Measurement method	-	-	-	AC bipolar method	-
	Measurement range	-	-	-	Cell constant 100 m^{-1}: 0.000 mS/m to 19.99 S/m	-
					Cell constant 10 m^{-1}: 0.0 µS/m to 1.999 S/m	
					Cell constant 1000 m^{-1}: 0.00 mS/m to 199.9 S/m	
	Repeatability	-	-	-	±0.5% F.S.±1 digit	-
Dissolved oxygen	Measurement method	-	-	-	-	Diaphragm galvanic battery method
	Measurement range	-	-	-	-	0.00 mg/L to 19.99 mg/L
	Repeatability	-	-	-	-	±0.1 mg/L±1 digit
Ambient temperature		0 to 45 °C				
Input CH		1		2		
Power supply		DC 3 V (LR6 dry cell battery) Option: AC adapter 100 to 240 V 50/60 Hz				
Power consumption		Approx. 0.03 W			Approx. 0.06 W	Approx. 0.03 W
Battery life		Approx. 200 hours			Approx. 100 hours	Approx. 200 hours
Mass of main unit (including dry cell batteries)		Approx. 300 g		Approx. 330 g		

The D-50 series has a compact waterproof body with numerous features. The main features are as follows:

1. Handiness

As conventional meters are too large for some people to carry in one hand, our main emphasis was on handiness such that the unit should be easily carried in one hand and so we reduced the size to 2/3 that of conventional units. To realize this size, we used a membrane switch for the switch section and separated the electrode holder from the main unit so that the electrode can be carried in a case.

2. Legibility

To make the measured value more legible, we used a display that is approximately 1.5 times larger than that of D-20 series. To show when electrode replacement is required, an electrode life indication was added in accordance with the sensitivity at the time of calibration.

3. Easy data handling (D-52, 53, 54, 55)

Conventionally an adapter has been required for connection to a PC, but the RS-232C port connection has enabled direct PC connection. Also, the main unit is capable of storing 300 data records and automatic data storage with a minimum interval of 2 seconds. These data can then be exported to a PC where a report can be created.

Benchtop pH Meter

During commercial production of the Benchtop F-50 series pH meter (F-52, 53, 54, 55), our investigations revealed that the most inconvenient points that customers are facing occur when actually using the pH meter. The majority of customers that anticipated problems were uneasy about possible electrode and sample measurement difficulties despite there actually being no significant problems. We therefore focused on how the unit should respond in case of difficulties. Aiming for a positive response when a problem occurs, we provided a human character for the pH meter, adding a sense of humor. The “Doctor” instructs with his know-how of pH measurement at turning on the character switch. Figure 2 shows a photo of the F-55 series, and Table 2 shows the main specifications of F-50 series.

Figure 2 The Model F-55

Table 2 Main Specifications of F-50 Series

		F-51	F-52	F-53	F-54	F-55
pH	Measurement method	Glass electrode method				
	Measurement range	pH 0.00 to 14.00	pH 0.000 to 14.000			
	Repeatability	±0.01 pH ±1 digit	±0.001 pH ±1 digit			
mV (ORP)	Measurement range	-1999 to1999	-1999.9 to1999.9			
	Repeatability	±1 mV ±1 digit	±0.1 mV ±1 digit			
Temperature	Measurement range	0.0 to 100.0 °C				
	Repeatability	±0.1 °C ±1 digit				
Ion	Measurement method	-	-	Ion selective electrode method	-	Ion selective electrode method
	Measurement range	-	-	0.00 µg/L to 999 g/L (mol/L)	-	0.00 µg/L to 999 g/L (mol/L)
	Repeatability	-	-	±0.5%F.S.±1 digit	-	±0.5%F.S.±1 digit
Conductivity	Measurement method	-	-	-	AC bipolar method	
	Measurement range	-	-	-	Cell constant 100 m^{-1}: 0.000 mS/m to 19.99 S/m	
					Cell constant 10 m^{-1}: 0.0 µS/m to 1.999 S/m	
					Cell constant 1000 m^{-1}: 0.00 mS/m to 199.9 S/m	
	Repeatability	-	-	-	±0.5% F.S.±1 digit	
Input CH		1	2			
Ambient temperature		0 to 45 °C				
Power supply		DC 6 V (LR6 dry cell battery) Option: AC adapter	AC adapter 100 to 240 V 50/60 Hz			
Power consumption		Approx. 0.024 W	Approx. 8.4 W			
Battery life		Approx. 500 hours	-			
Mass of main unit (including dry cell batteries)		Approx. 1 kg	Approx. 1.1 kg			

The main product features of F-50 series are as follows:

1. Color screen

For the first time a color screen has been adopted for a pH meter. In addition to the conventional digital display and graphic display, an analog-style indicator has been used for displaying the measured value (Figure 3).

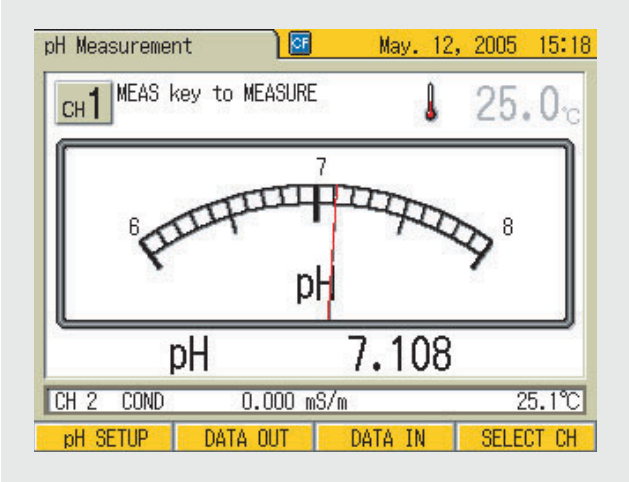

Figure 3 Analog-style Indicator

Going back more than ten years, pH meters were all equipped with analog indicators, and so many customers have strongly requested their return. Requiring no setup as the range is set automatically, this analog-style screen is suitable for checking for a stable indication condition, a feature requested by a number of customers.

The customer can select from seven display screen colors.

2. Navigation function

A character display shows the calibrated state after calibration, along with guidance for the standard solution measurement while calibrating. When the calibration is successful, “OK” is displayed (Figure 4), and the value of the calibrated standard solution, electric potential, and temperature are precisely displayed, so revealing the asymmetric potential and sensitivity. If the calibration fails, the cause of the failure is displayed and countermeasures are displayed by pressing the “Navi” key (Figure 5). This facilitates the operation if a problem occurs.

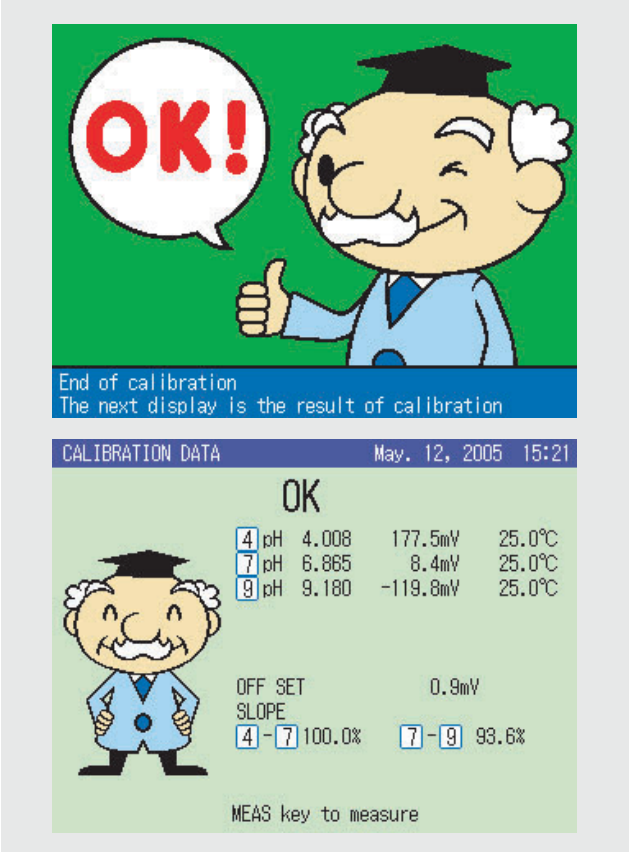

Figure 4 Display when Calibration has Succeeded

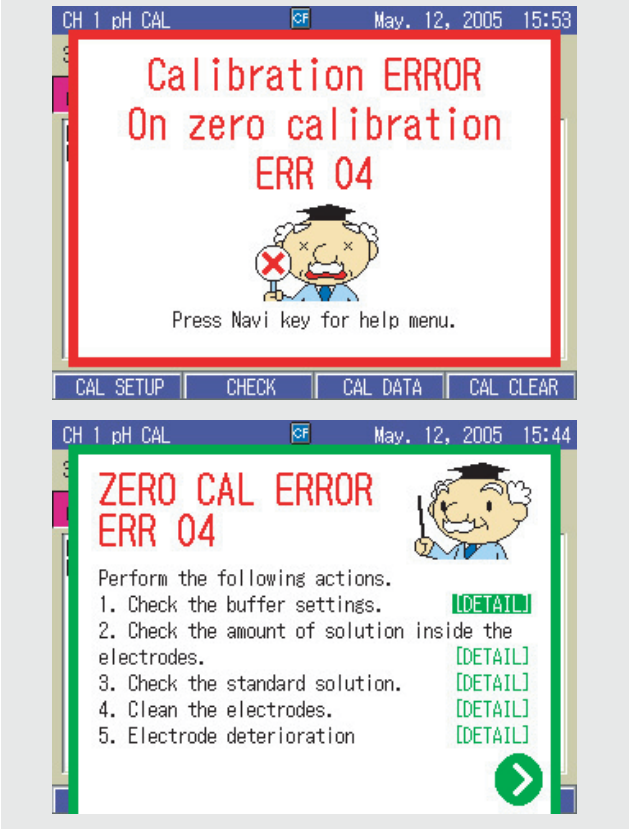

Figure 5 Display when Calibration has Failed

3. PC interface

All the models of F-50 series are equipped with a PC communication function through RS-232C. The high-end models are equipped with the world's first compact flash memory for a pH meter. With 16 MB memory preinstalled. Approximately 3000 measurements can be stored. Even though it may be impractical to carry the PC to the measurement site because the pH meter is normally used around water, easy data transfer is possible. Additionally the high-end models are equipped with a LAN networking connection, allowing communication of usage information to a PC.

PC Software

The PC software for both the D-50 series and the F-50 series is available to download free after customer registration on HORIBA's web site. This software allows easy retrieval of data stored in the pH meter and facilitates creating reports from this data.

The PC software for Part 11, the first software for pH meters conforming to the Part 11 regulation, was also produced as the PC software for F-55. The official name for Part 11 is FDA CFR 21 Part 11 issued by the U.S. Food and Drug Administration (FDA), which is a regulation for confirming reliable data and avoiding falsification of electronic records. It means the unit is equipped with a function for preventing electronic data from being falsified in order to correspond to this regulation. These functions enable introduction of the pH meter and its system to among others, the pharmaceutical industry with its stringent quality standards.

pH Checker

Recently a validation strategy for pH measurement has been in great demand. The meter's operation check is the key to this requirement. Previously, small and highly precise checkers did not exist. The pH checker X-51, provided with simulation outputs such as pH, temperature, ion, and dissolved oxygen, is produced with the 50 series. Furthermore, there is the X-52, with the conductivity simulation output only. Even personnel unfamiliar with the service technology can easily check the performance of a pH meter by using this checker with the F-50 series. The response can be definitely verified to Installation Qualification (IQ), Operational Qualification (OQ), Performance Qualification (PQ) required by the pharmaceutical industry and the wide range of industries that have started using this device.

Figure 6 shows the screen of F-50 series while checking using the pH checker.

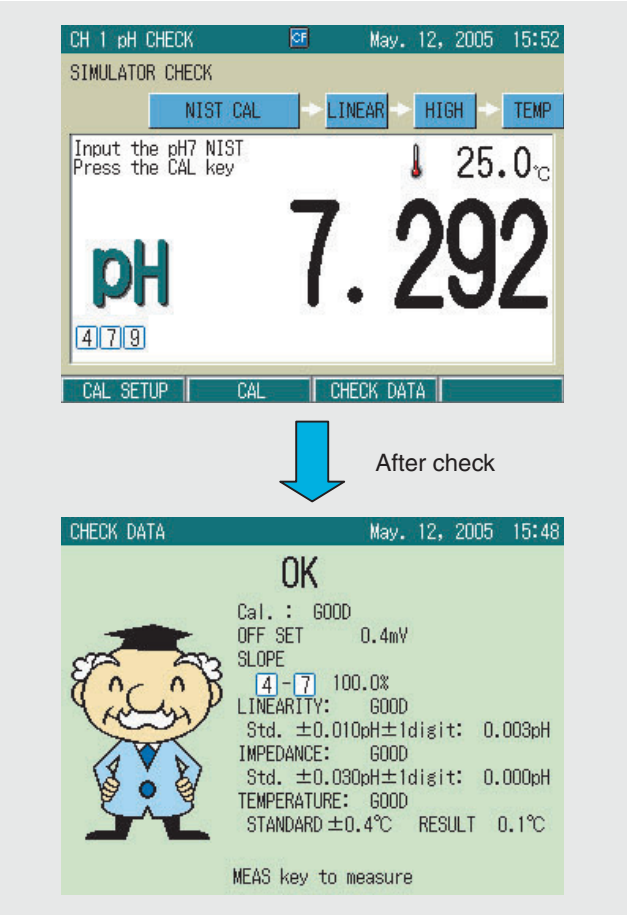

Figure 6 Screens during Checking

Glass Electrode

We developed the electrode using our long-term experience selling pH meters and to respond to customer requests as much as possible. After investigation, we found that costumers were not satisfied with the problem that different measured values are obtained when using two or more pH meters, which causes difficulties judging which value is true. Then we investigated the causes from various aspects, and found that particularly most problems were caused on the reference electrode side of the pH electrode. This is due to use of the silver-silver chloride inner electrode of the reference electrode, which results in silver outflow, clogging the liquid junction where the sample and inner solution contact. Therefore we built-in silver ion traps in all newly developed electrodes (Figure 7) to prevent the silver outflow from causing indication errors.

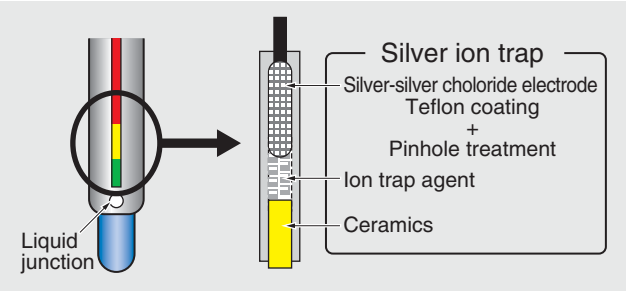

Figure 7 Ion Trap

The tip of the conventional glass electrode is made of thin glass membrane, therefore, the electrode had to be exchanged when the response section was broken. In the new product, the tip of the glass body electrode is made of thick membrane, and the structure has been changed so that the response section is located at the side. From this structural change, the glass electrode has been strengthened and improved. It has been released under the name of ToupH (Figure 8).

Figure 8 pH Waterproof Thick Membrane Glass Electrode ToupH

The sleeve type ToupH (9677-10D) electrode (Figure 9) has been produced for proteins and samples with high viscosity. It is suitable for this because the reference electrode liquid junction of the sleeve type reference electrode is washable.

Figure 9 Sleeve Type ToupH Electrode for Samples with High Viscosity

In addition, the micro ToupH (9669-10D) electrode (Figure 10) has also been produced as an electrode to measure small quantities of samples. The glass response membrane, reference electrode, and temperature electrode are mounted within an area of only 3 mm diameter to enable measurement of only 0.3 mL samples.

Figure 10 Micro ToupH Electrode for Small Amount Samples

A conventional micro electrode would hardly be able to measure correctly small amount samples due to influence of contamination or clogging of the silver-silver chloride inner electrode. The newly produced micro electrode adopts the ToupH glass, to maintain the same performance as that of the standard size one. The performance of the reference electrode is also drastically improved by mounting the silver ion trap. Some measured values from the conventional small amount electrode were abnormal due to bubbles generated inside the glass electrode. However the shape was modified to counter this so that the string (contact liquid line) is inserted to the tip of the inside of the glass electrode to maintain conductivity even if bubbles are generated. The result is popular among customers who wish to reduce the sample amount of valuable samples, and customers who are unable to measure due to small amount samples. So, we wish to continue with product development that utilizes HORIBA's electrode technologies. Table 3 shows the main specifications of electrodes.

Table 3 Main Specifications of Electrodes

	Waterproof thick membrane glass type ToupH electrode 9611-10D	Plastic body type electrode 9621-10D	ToupH electrode for samples with high viscosity 9677-10D	Micro electrode for small amount samples 9669-10D
Measurement temperature range (°C)	0 to 80	0 to 100 (Immersion measurement:0 to 50)	0 to 60	0 to 60
Storage temperature range (°C)	0 to 50	0 to 50	0 to 50	0 to 50
pH range	0 to 14	0 to 14	0 to 14	0 to 14
pH response glass	ToupH glass	Glass for low conductivity	ToupH glass	ToupH glass
Response membrane form	8 mm Tube type	6.4 mm Globular	8 mm Tube type	3 mm Tube type
Structure of refilling section of reference electrode inner solution	Sliding type	Sliding type	Sliding type	Sliding type
Liquid junction	Ceramics	Ceramics	Movable sleeve	Ceramics
Liquid junction material	Glass/ceramics	Glass/Silicone rubber/Ceramics/ Polysulfone/Polyacetal/ Polyimide/Polyamide/PVC	Glass	Glass/ceramics
Liquid junction diameter	12 mm	16 mm	12 mm	3 mm
Electrode length (including a cap)	150 mm	150 mm	150 mm	155 mm
Liquid junction height	18 mm	15 mm	26 mm	10 mm
Inner electrode	Ag/AgCl	Ag/AgCl	Ag/AgCl	Ag/AgCl
Silver ion trap	○	○	○	○
Inner solution of reference electrode	3.33 mol/L KCl	3.33 mol/L KCl	3.33 mol/L KCl	3.33 mol/L KCl
Max. immersion depth	-	1 m	-	-

ISFET Electrode

The ISFET electrode (0030-10D) (Figure 11), HORIBA's new product can be connected to conventional pH meters by inserting the required converter into the electrode grip. The tip of this electrode is pointed, which enables measurement by insertion into samples. Conventional glass is not used as the electrode material, therefore, it can be used at food processing sites where the presence of glass is prohibited.

Examples:

1) ISFET can perform on-the-spot measurement at food manufacturing sites. Conventional food pH measurement requires that the food is taken to a laboratory where it is crushed and extracted using water.
2) ISFET can measure by directly thrusting into ground soil, which enables soil measurement at multiple locations, requiring no water, whereas conventional methods use extracted samples of soil for pH measurement.

Figure 11 ISFET Electrode

Electrode Cleaning Solution

The electrode cleaning solution (#220) is a useful spin-off of the 50 series development. Hydrochloric acid is an effective conventional cleaning solution for the glass electrode when the pH electrode has deteriorated, because it removes dust from the glass surface, and thiourea solution is effective for the reference electrode because it removes the silver clogged silver on the inner electrode. However, it is difficult for most customers to condition solutions such as hydrochloric acid or thiourea solution. On the other hand, a number of evaluations were required for the life test of the cleaning solution as it must be verified first before coming into general use. For this product, we fixed a time of six months life from first manufacture to successful production. Although it is not a major product, we sincerely recommend this solution for cleaning the electrode in cases where calibration is not possible during use.

Conclusion

We have simultaneously developed a number of items including 16 types of main unit (including checkers), 4 types of electrode, and a cleaning solution. Despite a tightly scheduled development over a short period of approximately a year, we still received favorable feedback from our customers and so we felt somewhat satisfied with our work. We wish now to maintain this momentum of product development by continuing to listen to and consider our customers' comments.